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Title:
PRODUCTION OF PARTICULAR POLYESTERS USING A NOVEL CATALYST SYSTEM

Abstract:

This invention relates to a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.6 dL/g comprising reacting the diacid component with the diol component such that a combination of a titanium-based catalyst and a phosphorus-based catalyst is used during the polycondensation steps.

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(54) Title: PRODUCTION OF PARTICULAR POLYESTERS USING A NOVEL CATALYST SYSTEM (57) Abstract This invention relates to a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.6 dL/g comprising reacting the diacid component with the diol component such that a combination of a titanium-based catalyst and a phosphorus-based catalyst is used during the polycondensation steps.		

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**PRODUCTION OF PARTICULAR POLYESTERS
USING A NOVEL CATALYST SYSTEM**

Field of the Invention

5 This invention relates to a process for preparing modified or unmodified poly(ethylene terephthalate) using a titanium/phosphorus-based catalyst system.

Background of the Invention

10 Poly(ethylene terephthalate) may be derived from a process well known in the art comprising direct esterification of ethylene glycol and terephthalic acid. It may also be derived from a process comprising carrying out an ester interchange between ethylene
15 glycol and dimethyl terephthalate to form bis-2-hydroxy ethyl terephthalate which is polycondensed to poly(ethylene terephthalate) under reduced pressure and at elevated temperatures.

20 Problems have also been encountered in the manufacture of poly(ethylene terephthalate) by the ester interchange reaction and by direct esterification reaction. However, this material is slow with respect to ester interchange and is many times impractical with respect to commercial operations. Therefore, it is
25 typical to employ the use of a catalyst during these reactions.

 Typical catalyst or catalyst systems for polyester condensation are well-known in the art. For example, catalysts disclosed in U.S. Patent Nos. 4,025,492;
30 4,136,089; 4,176,224; 4,238,593; and 4,208,527, incorporated herein by reference, are deemed suitable in this regard. Further, R. E. Wilfong, Journal of Polymer Science, 54 385 (1961) sets forth typical catalysts which are useful in polyester condensation reactions.

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However, many of these catalysts do not produce finished polyester which has the desired clarity or color.

5 United States Patent 3,794,592 discloses a method of making polyesters suitable for use in making polyurethanes. More particularly, it discloses a method of making polyesters which have a reduced or controlled rate of reaction with isocyanates. Titanium may be used as a possible catalyst in the esterification and
10 transesterification reactions. Phosphoric acid may be added after the esterification or condensation reaction has been completed. The molecular weight of these products are from about 500 to 10,000 and would not be useful in molding applications.

15 United States Patent 3,907,754 discloses a catalyst system for the production of poly(ethylene terephthalate) which comprises, in combination, salts of manganese and cobalt with acetyl triisopropyl titanate and a phosphate ester.

20 United States Patent 4,260,735 discloses the use of an alkanolamine titanium chelate catalyst to esterify and polycondense aromatic polycarboxylic acids or anhydrides, such as terephthalic acid, with a glycol, such as ethylene glycol, at low glycol to acid reactant
25 ratios. The objective of this invention is to make possible commercial production of polyesters with low ether contents, without the addition of any inhibitor to suppress formation of DEG.

30 United States Patent 4,150,215 discloses a process for preparing high molecular weight polyester resins by reacting ethylene glycol with terephthalic acid in the absence of a catalyst and polymerizing the product under solid state polymerization condition.

35 United States Patent 3,962,189 discloses a catalyst-inhibitor system for the polymerization of

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poly(ethylene terephthalate) comprising a combination of organic or inorganic salts of manganese and cobalt, titanium alkoxides, organic salts of alkali metals, or alkaline earth metals, and a phosphate ester.

5 United States Patent 4,356,299 discloses a poly(ethylene terephthalate) polycondensation catalyst system comprising a catalyst metal in the form of an alkyl titanate and an antimony compound.

10 Previously, the catalyst systems useful for making poly(ethylene terephthalate) of the prior art employed titanium-based catalysts, phosphorus-based compounds, usually in combination with manganese and/or antimony.

Therefore, there has been a need in the art to have a catalyst system which speeds up the reaction so that
15 it is useful for economical purposes and for making a range of molecular weights useful for molding purposes but which also results in a condensation polymer having good clarity and color. Furthermore, environmental concerns demand that the level of catalyst metals be
20 decreased or minimized which is achieved by using the process or this invention.

Heretofore, a catalyst system containing low amounts of one or more alkyl titanates in combination with a phosphorus-based compound in order to make
25 poly(ethylene terephthalate) or modified poly(ethylene terephthalate) of sufficient molecular weight to be useful in molding applications has been unknown.

Summary of the Invention

30 This invention involves the use of a catalyst system which has the advantages of the prior art with respect to the catalyst system which promotes esterification or transesterification and polycondensation and molecular weight buildup while
35 maintaining good color and clarity.

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This invention relates to a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g comprising:

5 reacting a diacid component further comprising
at least 65 mole % terephthalic acid or a diester
component comprising at least 65 mole % $C_1 - C_4$
dialkyl terephthalate and a diol component
comprising at least 65 mole % ethylene glycol at
10 temperatures to effect steps (A) and (B) as
follows:

(A) esterification or transesterification,
wherein said esterification is carried
out, optionally, in the presence of about
15 1 to about 50, preferably 1 to 20, more
preferably 1 to 10 parts of titanium
present in the form of an alkyl titanate
or

optionally, in the presence of a
20 catalyst system comprising from
about 1 to about 50, preferably 1 to
20, more preferably 1 to 10 parts of
titanium present in the form of an
alkyl titanate and from about 1 to
25 about 100, preferably 1 to 50, more
preferably 1 to 30, even more
preferably 1 to 15 parts of
phosphorus in the form of a
phosphate ester or phosphoric acid,
30 and

wherein said transesterification is
carried out in the presence of from about
1 to about 50 parts of titanium in the
form of an alkyl titanate; and

- 5 -

(B) polycondensation, wherein said polycondensation is carried out in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid; each of the parts of the catalyst representing per million parts of polymer product, wherein the mole percentage for all of the diacid component totals 100 mole %, and wherein the mole percentage for all of the diol component totals 100 mole %.

In another embodiment of the invention, the process incorporates the use of either an inorganic toner system comprising salts of cobalt and/or an organic toner system comprising about 1 to about 10 ppm of at least one copolymerizable 6-arylamino -1-cyano-3H-dibenz [f,i]isoquinoline-2,7-dione or at least one copolymerizable blue 1,4-bis(2,6-dialkylanilino) anthraquinone compound in combination with at least one red anthraquinone or anthrapyridone (6-arylamino-3H-dibenz[f,i]isquinoline-2,7-dione) compound at a temperature to effect esterification or ester interchange and polycondensation in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid, each of the parts of one catalyst system being per million parts at polymer product and the diacid or diester component totaling 100 mole % and the diol component totaling 100 mole %.

Some of the advantages of this invention over the prior art are that: (1) it employs the use of a catalyst

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system containing low amounts of one or more alkyl titanates in combination with a phosphorus-based compound in order to make poly(ethylene terephthalate) or modified poly(ethylene terephthalate) of sufficient molecular weight to be useful in molding applications, (2) the product has good clarity (less haze) and color, (3) there is a lower amount of metal and acetaldehyde in the final product and (4) obtaining a slow crystallization rate in poly(ethylene terephthalate) or modified poly(ethylene terephthalate).

Detailed Description of the Preferred Embodiments

This invention involves a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g, preferably greater than 0.70 dL/g, comprising reacting a diacid or diester component comprising at least 65 mole % terephthalic acid or C₁ - C₄ dialkylterephthalate, preferably at least 70 mole %, more preferably at least 75 mole %, even more preferably, at least 95 mole %, and a diol component comprising at least 65 mole % ethylene glycol, preferably at least 70 mole %, more preferably at least 75 mole %, even more preferably at least 95 mole %. It is also preferable that the diacid component is terephthalic acid and the diol component is ethylene glycol. The mole percentage for all of the diacid component totals 100 mole %, and the mole percentage for all of the diol component totals 100 mole %.

After melt and/or solid phase polycondensation the polyesters have an inherent viscosity (I.V.) of about 0.65 to about 1.2 dL/g, preferably 0.75 dL/g measured at 25°C in a 60/40 ratio by weight of phenol/tetrachloroethane.

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Where the polyester components are modified by one or more diol components other than ethylene glycol, suitable diol components of the described polyesters may be selected from 1,4-cyclohexanedimethanol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 2,8-bis(hydroxymethyl)-tricyclo-[5.2.1.0]-decane wherein Z represents 3, 4, or 5; and diols containing one or more oxygen atoms in the chain, e.g., diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol and the like. In general, these diols contain 2 to 18, preferably 2 to 8 carbon atoms. Cycloaliphatic diols can be employed in their cis or trans configuration or as mixtures of both forms. A preferred modifying diol component is 1,4-cyclohexanedimethanol.

Where the polyester components is modified by one or more acid components other than terephthalic acid, the suitable acid components (aliphatic, alicyclic, or aromatic dicarboxylic acids) of the linear polyester may be selected, for example, from isophthalic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecanedioic acid, 2,6-naphthalenedicarboxylic acid and the like. In the polymer preparation, it is often preferable to use a functional acid derivative thereof such as the dimethyl, diethyl, or dipropyl ester of the dicarboxylic acid. The anhydrides or acid halides of these acids also may be employed where practical.

The linear polyesters may be prepared according to polyester forming conditions well known in the art. The reaction should occur at a temperature to effect esterification and polycondensation. For example, a

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mixture of one or more dicarboxylic acids, preferably aromatic dicarboxylic acids, or ester forming derivatives thereof, and one or more diols may be heated in the presence of esterification and/or

5 transesterification catalysts at temperatures in the range of about 150° to about 300°C, preferably, about 200°C to about 300°C, and even more preferably, about 260°C to about 300°C, and pressures of atmospheric to about 0.2 mm Hg. Normally, the dicarboxylic acid is

10 esterified with the diol(s) at elevated pressure and at a temperature at about 240°C to about 270°C. Polycondensation then is effected by increasing the temperature and lowering the pressure while excess diol is removed from the mixture.

15 The reaction is carried out at a temperature to effect esterification or ester interchange and polycondensation in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium in the form of an alkyl titanate and from about 1 to about

20 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid, each of the parts of the catalyst system representing per million parts of polymer product and the diacid or diester component totaling 100 mole % and the diol component totaling 100 mole %.

25 Alkyl titanates useful within the context of this invention include: acetyl triisopropyl titanate, titanium tetraisopropoxide, titanium glycolates, titanium butoxide, hexyleneglycol titanate, tetraisooctyl titanate, titanium tetramethylate,

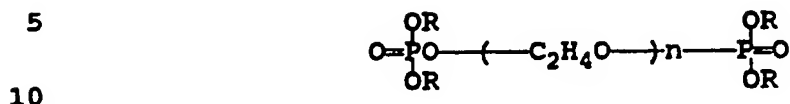
30 titanium tetrabutylate, titanium tetra-isopropylate, titanium tetrapropylate, tetrabutyl titanate, and the like. A preferred alkyl titanate is acetyl triisopropyl titanate.

The preferred phosphorus-based compound is a

35 phosphate ester.

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It is more preferred that the phosphate ester has the formula



wherein n has an average value of 1.5 to about 3.0 with about 1.8 being most preferred and each R is hydrogen or an alkyl radical having from 6 to 10 carbon atoms with octyl being most preferred, the ratio of the number of R groups or hydrogen atoms to the number of phosphorus atoms being about 0.25 to 0.50 with about 0.35 being most preferred; and the ester having a free acidity equivalent of about 0.2 to 0.5.

Other phosphate esters useful in this invention include ethyl acid phosphate, diethyl acid phosphate, triethyl acid phosphate, arylalkyl phosphates, tris-2-ethylhexyl phosphate and the like.

Another preferred phosphorus-based compound is phosphoric acid.

It is preferred that the catalyst system of the invention comprises about 3 to about 10 parts of catalyst metal in the form of tetraisopropyl titanate and from about 5 to about 15 parts of phosphorus in the form of said phosphorus-based compound.

It is preferred in the process of this invention that the catalyst system further comprises an inorganic toner or an organic toner. Where the toner is an inorganic one, salts of cobalt are preferred. The cobalt toner is usually added after the esterification step before polycondensation when a diacid is reacted. In the case of the reaction at a diester, the toner may

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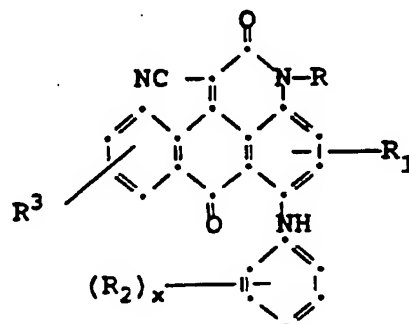
be present during transesterification and during the polycondensation step.

Examples of suitable cobalt salts are cobaltous acetate trihydrate, cobaltous nitrate, cobaltous chloride, cobalt acetylacetonate, cobalt naphthenate, and cobalt salicyl salicylate and cobalt acetate. It is preferred that the salt of cobalt is cobalt acetate.

When the cobalt salt is cobalt acetate, it is preferable that the cobalt acetate is present in the amount of 10-120 ppm Co, the acetyl triisopropyl titanate is present in the amount of 1-50 ppm Ti, and the phosphorus-based compound is present in the amount of 1-100 ppm phosphorus, all parts by weight based on the total weight of the polymer.

Where the toner is an organic one, it is preferred that the toner is an organic toner system comprising about 1 to about 10 ppm of at least one copolymerizable 6-arylamino -1-cyano-3H-dibenz[f,ij]isoquinoline-2,7-dione or at least one copolymerizable 1,4-bis(2,6-dialkylanilino) anthraquinone compound in combination with at least one bis anthraquinone or bis anthrapyridone(6-arylamino-3H-dibenz[f,ij]isoquinoline-2,7-dione) compound, wherein the organic toners contain at least one, preferably two polyester reactive groups.

A preferred organic toner comprises at least one 6-arylamino-1-cyano-3H-dibenz[f,ij]isoquinoline-2,7-diones having the formulae



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wherein

R is hydrogen, cycloalkyl, allyl, alkyl, aryl, aralkyl, alkoxyalkyl or cycloalkylalkylene;

5 R_1 is hydrogen, halogen, alkyl, alkoxy, aryloxy, alkylthio or arylthio;

R_2 is hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, carbalkoxy, carbaryloxy, carbaralkoxy, carboxy, sulfamoyl, alkylsulfamoyl, dialkylsulfamoyl, alkylarylsulfamoyl, cycloalkylsulfamoyl, arylsulfamoyl, carbamoyl, alkylcarbamoyl, dialkylcarbamoyl, alkylarylcarbamoyl, cycloalkylcarbamoyl, arylcarbamoyl, 2-pyrrolidono, acylamido, or N-alkylacylamido;

10 R_3 is one or more residues selected from the group consisting of hydrogen, halogen, alkyl and alkoxy; and

15

 x is an integer of 1 to 5; wherein one or more of the alkyl, alkoxy, alkoxy, aryl, aryloxy, alkylthio, arylthio or aralkyl residues may contain one or more reactive groups selected from the group consisting of carboxy, carbalkoxy, carbaryloxy, N-alkyl-carbamoyloxy, carbamoyloxy, acyloxy, chlorocarbonyl, hydroxyl, cycloalkylcarbonyloxy, N-arylcarbamoyloxy and N,N-dialkylcarbamoyloxy and wherein said alkyl and aryl groups may contain substituents selected from the group consisting of alkoxy, acyloxy, cyano, hydroxy, halogen and acylamido; wherein at least one polyester reactive group is present to permit copolymerization. These toners are disclosed in United States Patent 4,754,174, which is

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incorporated herein by reference in its entirety.

Even more preferably, the organic compound useful in this invention when copolymerized is

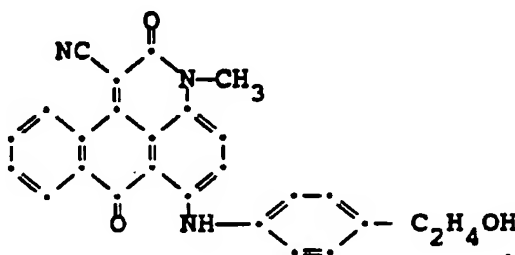
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The preferred organic toner system of this invention are certain blue substituted 1,4-bis(2,6-dialkylanilino) anthraquinones in combination with selected red anthraquinone and anthrapyridone (3H-dibenz[fi,j]isoquinoline-2,7-dione) compounds as disclosed in United States Patent 5,372,864 which is hereby incorporated by reference in its entirety.

35

More particularly, this organic toner system is comprised of at least one blue 1,4-bis(2,6-dialkylanilino) anthraquinone(s) of formula (I):

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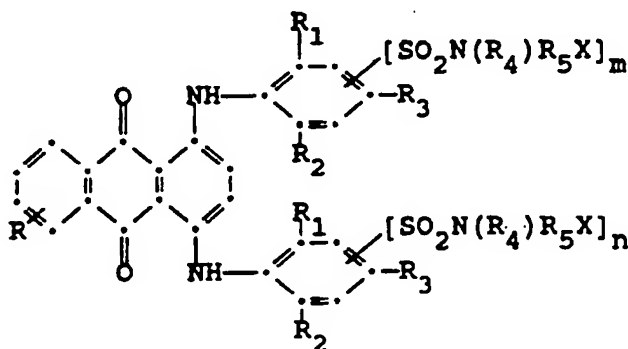
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(I)

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wherein:

R is selected from the group consisting of hydrogen, C₁-C₆ alkyl, halogen, carboxy, and C₁-C₆

alkoxy-C(=O)-;

R₁ and R₂ are independently C₁-C₆-alkyl;

R₃ is selected from the group consisting of hydrogen, halogen, C₁-C₆-alkyl, substituted C₁-C₆ alkyl, hydroxy, C₁-C₆-alkoxy, substituted C₁-C₆-alkoxy, cyano, thiocyno, C₁-C₆-alkylthio, substituted C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, substituted C₁-C₆-alkylsulfonyl, C₁-C₆-alkoxycarbonyl, carboxy, aryloxy, arylthio, arylsulfonyl, and SO₂N(R₄)R₅X when m and/or n are zero;

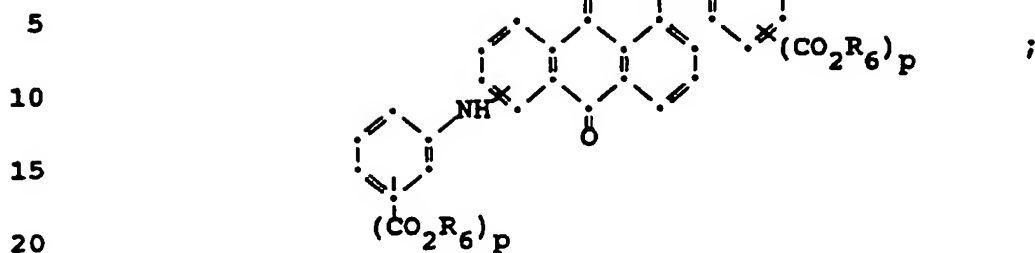
R₄ is selected from the group consisting of hydrogen, C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₃-C₈-alkenyl, C₃-C₈-alkynyl, C₃-C₇-cycloalkyl and aryl;

R₅ is a linking group selected from the group consisting of C₁-C₆-alkylene, C₁-C₆-alkylene-Z-C₁-C₆-alkylene, arylene-C₁-C₆-alkylene, arylene-Z-C₁-C₆-alkylene, C₃-C₇-cycloalkylene, C₁-C₆-alkylene-cycloalkylene-C₁-C₆-alkylene, C₁-C₆-alkylene-arylene-C₁-C₆-alkylene, and C₁-C₆-alkylene-Z-arylene-Z-C₁-C₆-alkylene, wherein Z is selected from -O-, -S- or SO₂;

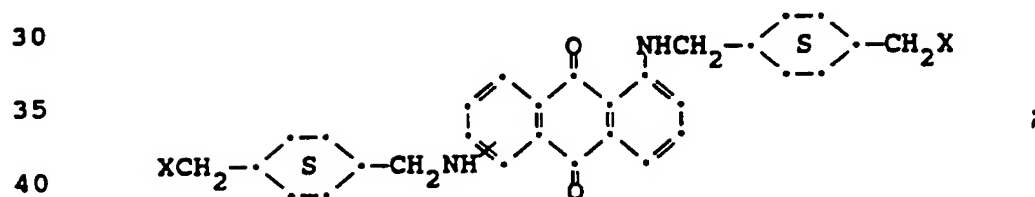
X is hydrogen or a polyester reactive group; and m and n are independently 0 or 1; with the proviso that at least one polyester reactive group is present.

The red components which may be blended with blue components of formula I above have the following structural formulae II - X:

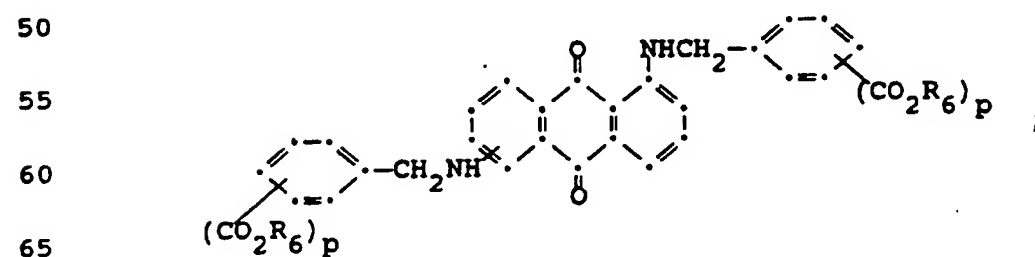
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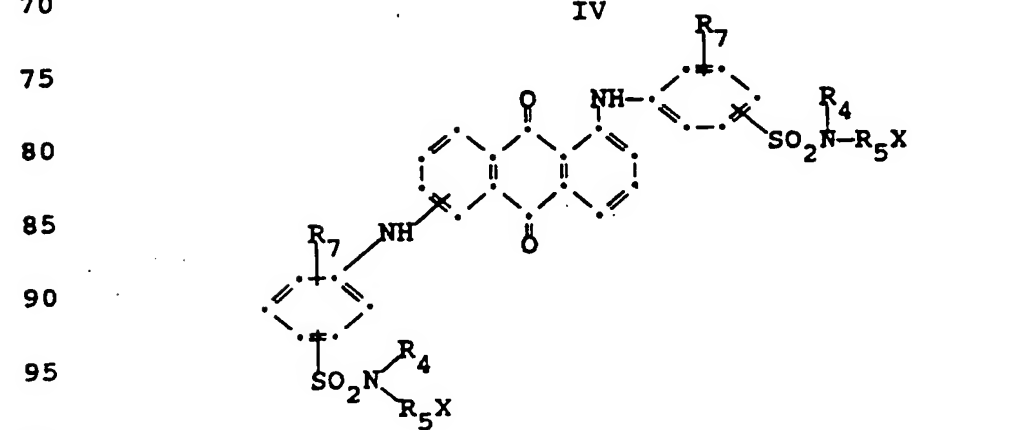
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III

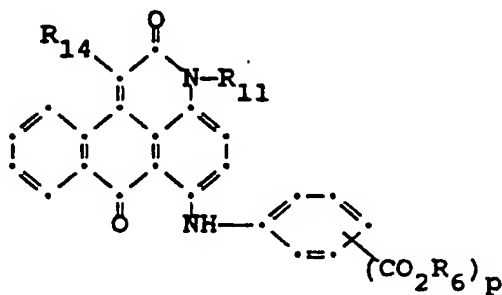
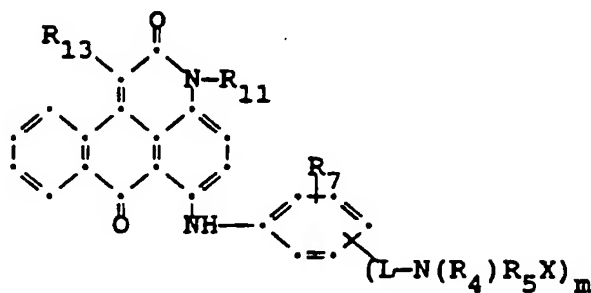
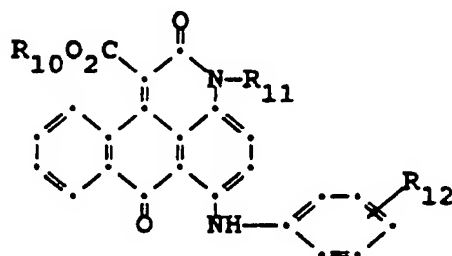
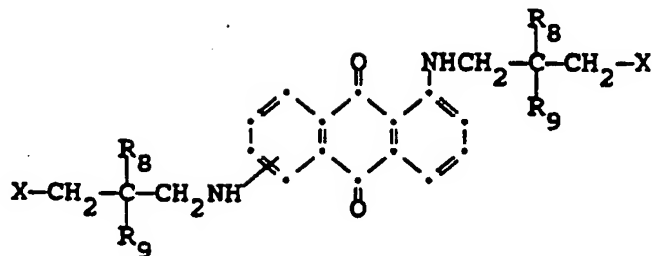


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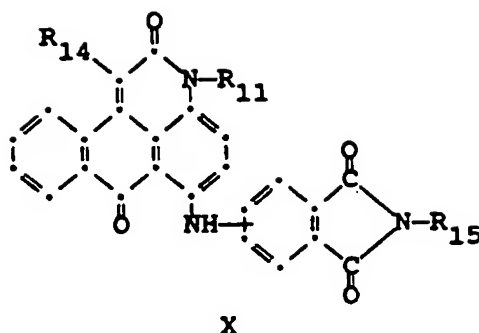
V

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wherein:

R_6 is selected from the group consisting of hydrogen, C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_3 - C_7 -cycloalkyl or aryl;

R_7 is hydrogen or one to three groups selected from C_1 - C_6 -alkyl, substituted C_1 - C_6 alkyl, C_1 - C_6 -alkanoylamino, halogen, hydroxy C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio;

R_8 and R_9 are the same or different and are selected from the group consisting of C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_3 - C_7 -cycloalkyl or aryl;

R_{10} is selected from the group consisting of C_1 - C_6 -alkyl, C_3 - C_7 -cycloalkyl or aryl;

R_{11} is selected from the group consisting of hydrogen, C_1 - C_{12} -alkyl, substituted C_1 - C_{12} -alkyl, C_3 - C_7 -cycloalkyl and aryl;

R_{12} is hydrogen or one to three groups selected from the group consisting of C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, substituted C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, substituted C_1 - C_6 -alkylthio, halogen, hydroxy, C_1 - C_6 -alkanoylamino, aroylamino, C_1 - C_6 -alkyl-sulfonylamino and arylsulfonylamino;

R_{13} and R_{14} are selected from hydrogen, cyano or CO_2R_{10} ;

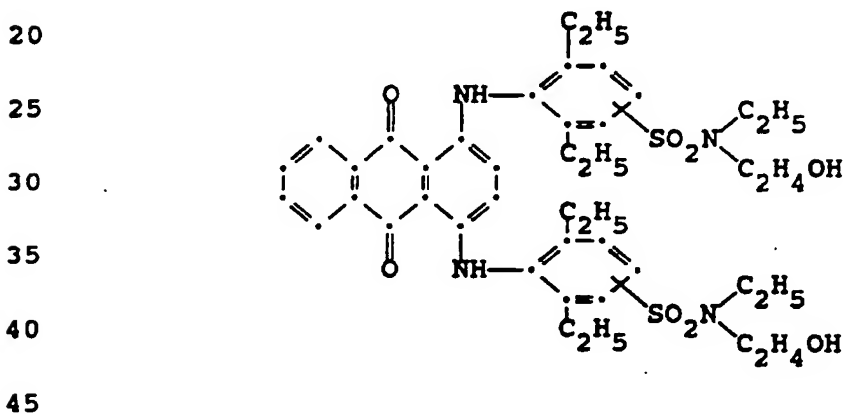
R_{15} is R_4 or R_5X as previously defined;

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L is $-\text{CO}-$ or $-\text{SO}_2-$; X is as previously defined; m is 0 or 1; p is 1 or 2; with the provisos that R_{13} is hydrogen when m is 0 and at least one polyester reactive group is present.

5 In a preferred embodiment, the blue anthraquinone compound(s) correspond to structure (I) above, wherein R is hydrogen; R_1 and R_2 are independently selected from methyl and ethyl; R_3 is hydrogen, methyl, or bromo; R_4 is hydrogen, C_1 - C_4 -alkyl or aryl; R_5 is selected from
 10 the group consisting of C_1 - C_6 -alkylene, C_1 - C_4 -alkylene- O - C_1 - C_4 -alkylene, $-\text{CH}_2\text{C}_6\text{H}_{10}\text{CH}_2-$, arylene, or $-\text{CH}_2$ -alkylene- and the red component corresponds to formula (V), wherein R_7 is C_1 - C_6 -alkoxy and R_4 and R_5 are as defined in claim 1.

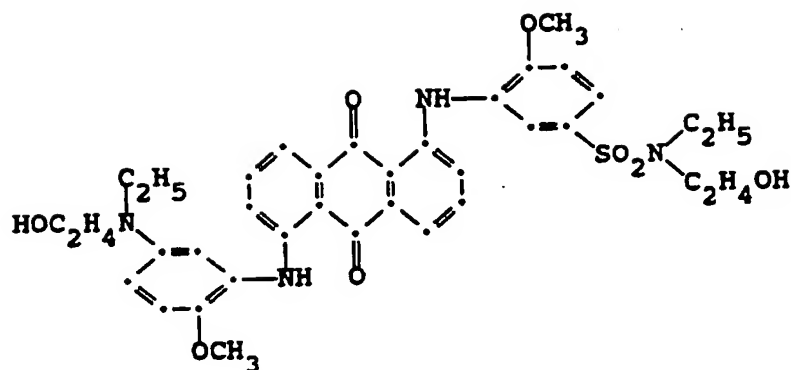
15 In an especially preferred embodiment of the present invention, the blue compound of formula (I) is



50 and the red compound of formula (V) is

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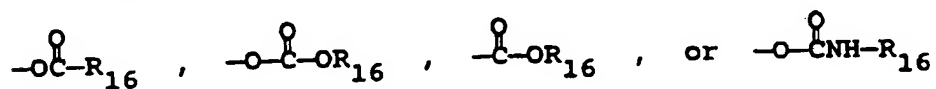
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In a further preferred embodiment, the concentration of blue and red compounds taken together is from about 0.5 ppm to about 10 ppm. Most preferably, the total concentration of blue compound is 1 to 7 ppm and total concentration of red compound is 0.5 to 3 ppm.

The term "polyester reactive group" is used herein to describe a group which is reactive with at least one of the functional groups from which the polyester is prepared under polyester forming conditions. Examples of the groups which X may represent include hydroxy, carboxy, an ester group, amino, C₁-C₆-alkylamino, etc. The ester radicals may be any radical having the formulae

45



50

wherein R₁₆ is selected from the group consisting of C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₃-C₇-cycloalkyl or aryl. Reactive group X is preferably hydroxy, carboxy, C₁-C₂-alkoxycarbonyl or acetoxy.

In the terms "substituted C₁-C₆-alkyl", "substituted C₁-C₁₂-alkyl", "substituted C₁-C₆-alkoxy", "substituted C₁-C₆-alkylthio", "substituted C₁-C₆-alkylsulfonyl", "C₁-C₆-alkylsulfonylamido", "substituted

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- 19 -

alkylene", "C₁-C₆-alkoxycarbonyl", the alkyl and
 alkylene groups or portions of the groups may contain as
 further substituents one or more groups, preferably one
 to three groups selected from the group consisting of
 5 hydroxy, halogen, cyano, aryl, aryloxy, arylthio,
 C₁-C₄-alkylthio, C₁-C₄-alkylthio, C₃-C₇-cycloalkyl,
 C₁-C₄-alkanoyloxy and $-(O-R_{17})_p-R_{18}$, wherein R₁₇ is
 selected from the group consisting of C₁-C₆-alkylene,
 C₁-C₆-alkylenearylene, cyclohexylene, arylene, and
 10 C₁-C₆-alkylenecyclohexylene; R₁₈ is selected from the
 group consisting of hydrogen, hydroxy, carboxy, C₁-C₄-
 alkanoyloxy, C₁-C₄-alkoxycarbonyl, aryl, and C₃-C₇-
 cycloalkyl; and p is 1, 2, 3, or 4.

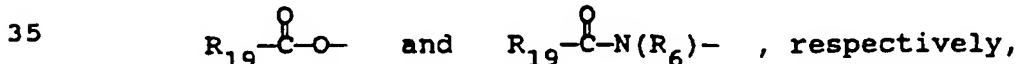
The term "aryl" as used herein preferably denotes
 15 phenyl and phenyl substituted with one to three
 substituents selected from the group consisting of
 C₁-C₆-alkyl, C₁-C₆-alkoxy, halogen, carboxy, cyano,
 C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, trifluoromethyl,
 hydroxy, C₁-C₆-alkanoyloxy, C₁-C₆-alkanoylamino, and
 20 C₁-C₆-alkoxycarbonyl.

The term "arylene" includes 1,2-, 1,3- and
 1,4-phenylene and such radicals substituted one to three
 times with C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-alkoxy-
 carbonyl, or halogen.

25 The terms "C₃-C₈-alkenyl" and "C₃-C₈-alkynyl" are
 used to denote aliphatic hydrocarbon moieties having 3-8
 carbons and containing at least one carbon-carbon double
 bond and one carbon-carbon triple bond, respectively.

The term "halogen" is used to indicate bromine,
 30 chlorine, fluorine, and iodine.

The terms "C₁-C₆-alkanoyloxy" and "C₁-C₆-alkanoyl-
 amino" are used to represent radicals of the formulae



- 20 -

5 wherein R_{19} is a straight or branched chain C_1 - C_6 -alkyl radical and R_6 is as defined above.

Thus, the present invention provides a molding or fiber grade polyester preferably having copolymerized therein, in an amount sufficient to improve the apparent
10 whiteness and/or clarity of the polyester, a blue 1,4-bis(2,6-dialkylanilino)anthraquinone compounds of Formula (I) plus a red anthraquinone or anthrapyridone compounds of formulae (II) - (X) above. In this regard, the blue and red compounds will not be present in an
15 amount sufficient to impart a substantial amount of color to the polyester.

The organic toners may be added before the esterification, transesterification or polycondensation steps. As a further aspect of the present invention,
20 the method provided herein also involves the step of imparting clarity to the poly(ethylene terephthalate) or modified poly(ethylene terephthalate) of the invention.

In yet another aspect of the invention, there is provided in the method of polymerization, in the melt,
25 of an aromatic polycarboxylic acid or anhydride with a glycol using titanium compound catalysts to form high molecular weight linear polymers, the improvement comprising

(a) esterifying the acid or anhydride with the
30 glycol in the presence or absence of from about 1 ppm of Ti to about 50 ppm of Ti as an alkyl titanate at a temperature of between about 197°C and about 300°C. for a period of from about 0.5 hours to about 7 hours at a pressure of between about 0 psig and about 100
35 psig at a molar ratio of glycol to acid or anhydride of about 1.1:1 to about 3:1,

- 21 -

- 5 (b) further reacting and polycondensing the product of step (a) which contains the above mentioned titanium catalyst, in contact with a phosphorus based compound at about 1 to about 100 ppm phosphorus at a temperature of from about 250 to 310°C, under vacuum of from about 0.1 Torr to about 200 Torr for a period of from about 0.5 hour to 12.0 hours while removing the products of condensation so that the resulting polymer has an intrinsic viscosity between about 0.4 to about 1.2 and contains less than 5 percent by weight diethylene glycol, without adding a diethylene glycol inhibitor, with each of the parts of the compound being per million parts of the first polymer product and
- 10 (c) further polycondensing the crystallized product of step (b) in the solid-state and in the presence of countercurrent inert gas or under vacuum and at elevated temperatures of from about 200°C to about 235°C for 2 - 24 hours.

25 Molded articles or fibers can be prepared from the product of the invention. Containers are the preferred molded article.

As noted above, the toner blends of the present invention can be added before or during polymerization.

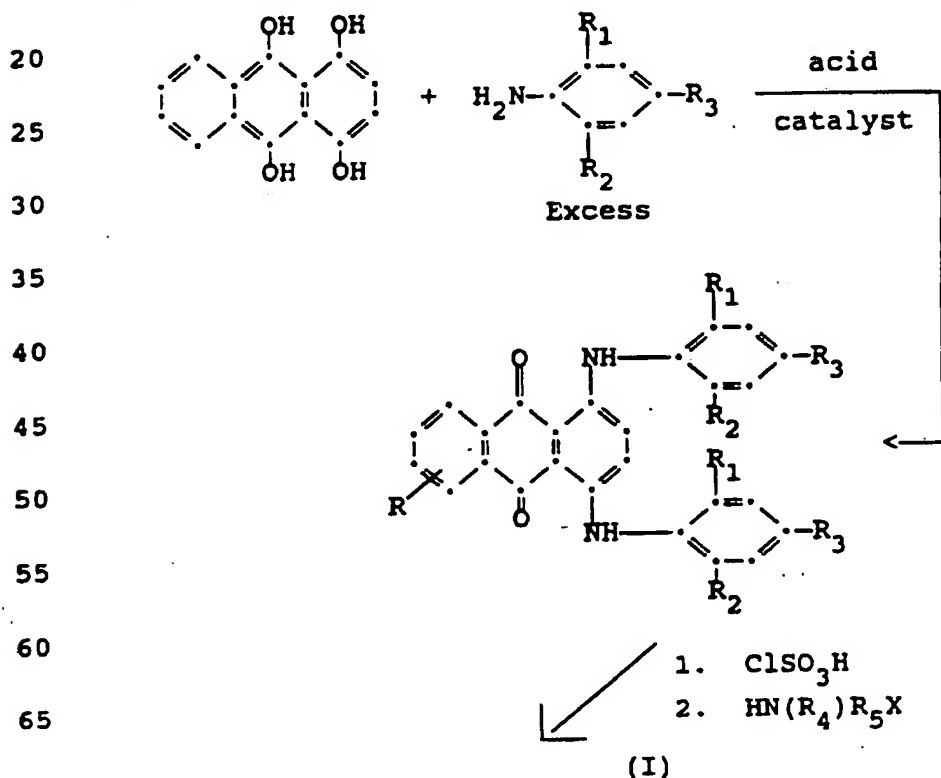
Accordingly, as a further aspect of the present invention, there is provided a premix composition comprising a blend of at least one blue 1,4-bis(2,6-dialkylanilino)anthraquinone compound of formula (I), along with a red anthraquinone or anthrapyridone compound of formulae (II) - (X) above. The premix composition may be a neat blend of the red and blue compounds or the composition may be

- 22 -

pre-dissolved in one of the polyester's monomeric species, e.g., ethylene glycol.

The total amount of toner components added depends, of course, on the amount of inherent yellow color in the polyester. Generally, a maximum concentration of about 10 ppm of combined toner components and a minimum concentration of about 0.5 ppm are required with about 1 - 7 ppm of blue component (I) in combination with about 0.5 - 3 ppm of red components of formulae (II - X) being preferred.

The blue anthraquinones of formula (I) can be prepared in general by reaction of leuco quinizarin (1,4,9,10-tetrahydroxyanthracene) compounds with an excess of aromatic amines, preferably in the presence of acid catalysts such as boric acid as described in U.S. Patent No. 3,918,976, incorporated herein by reference and as follows:



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The 1,4-bis(2,6-dialkylanilino)anthraquinone compounds thus produced are readily functionalized if needed by first chlorosulfonating with chlorosulfonic acid to produce di-sulfonyl chlorides which can be reacted with amines containing polyester reactive groups, the general method being disclosed in U.S. Patent No. 2,731,476, incorporated herein by reference.

Typical amines corresponding to formula $\text{HN}(\text{R}_4)\text{R}_5\text{X}$ include 2-aminoethanol, 2,2-iminodiethanol, 1-amino-2,3-propanediol, 2-methylaminoethanol, 2-ethylaminoethanol, 2-anilinoethanol, methyl anthranilate, methyl m-amino benzoate, p-aminobenzoic acid, m-aminophenol, 6-amino-hexanoic acid, β -alanine, glycine ethyl ester, 2-(p-aminophenyl)ethanol, 2-(p-aminophenoxy)ethanol 4-aminomethylcyclohexane methanol and 3-amino-2,2-dimethyl-1-propanol.

Red compounds (II) can be prepared by reacting 1,5-dichloroanthraquinone and/or 1,8-dichloroanthraquinone or mixtures thereof with o, m- and p-aminobenzoic acids (and esters thereof) by a modified Ullmann reaction involving nitrogen arylation of the anilines in the presence of copper catalysts (see U.S. Patent No. 4,359,580, incorporated herein by reference).

Red compounds of formula (III) can be prepared as described in U.S. Patent No. 4,420,581 and compounds of formula (VI) can be prepared as in U.S. Patent No. 4,999,418, incorporated herein by reference.

Red anthraquinone compounds of formula (IV) can be prepared by reacting 1,5-dichloroanthraquinone and 1,8-dichloroanthraquinone or mixtures thereof with substituted benzyl amines by procedures similar to those used in preparing compounds of formulae (III) and (VI).

Red anthrapyridone compounds (VII) can be prepared as disclosed in U.S. Patent No. 4,790,581 incorporated

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herein by reference; procedures useful in preparing red-violet anthrapyridone compounds (VIII) and (IX) are disclosed in U.S. Patent No. 4,745,174, incorporated herein by reference.

5 Haze half-times are defined as the time after the start of crystallization of a material when the level of haze becomes such that the amount of light transmitted through a film of the sample reaches half of its maximum value. This halftime is roughly the same as the
10 crystallization half-times known in the art. Examples of measurements of crystallization half-times are disclosed in J. Polymer Sci. A2, Vol. 6 (1962) by Adams and Stein.

 A haze half time test has been found to be useful
15 in determining haze results in molded preforms. It has been found to be an excellent measure of crystallization rate with respect to bottle polymer applications. Polymers with higher haze half times are less likely to contain haze in preforms. In this test, a hazemeter is
20 used to measure the light absorbance of a molten polymer film as it crystallizes and becomes more turbid (hazy); the resulting turbidity verses time data are analyzed to obtain a half time. The haze half time test has been used to measure the crystallization rate in the
25 experimental section as follows below. This invention involves a process for preparing polyesters having a slow crystallization rate, using TPA as the primary source of the terephthalate moiety, long melt phase polycondensation times, and a catalyst system as
30 described herein.

 The haze half-times referred to in the following examples are measured by method described as follows:

 The polymer sample (a fine powder) is melted for about 20 seconds between 2 aluminum blocks heated to
35 about 280°C. The sample is transferred to a set of 2

- 25 -

aluminum blocks heated to about 130°C. Light is transmitted from a projector lamp which is sent through the sample as it crystallizes isothermally and the light intensity is measured using a photodetector. The photodetector signal is recorded using a computer and is analyzed to determine the time after the start of crystallization when the level of haze becomes such that the amount of light transmitted through a film of the sample reaches half of its maximum.

Polymer prepared using this process has a significantly higher haze half time than polymer prepared by conventional processes such as antimony (Sb) based catalyst combined with phosphorus (see attached Table 1). Polymer prepared by the process described in this invention is useful for obtaining poly(ethylene terephthalate) or modified poly(ethylene terephthalate) with a slow crystallization rate for molding haze free preforms which are used to blow mold bottles of different sizes.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated. The starting materials are commercially available unless otherwise indicated.

EXAMPLES

Example 1 - Preparation of Terephthalic Acid (TPA) Based Oligomer

Ethylene glycol (450 lbs) was placed in a paste preparation vessel. The agitator of the vessel was started. TPA powder (1050 lbs) was added slowly at a rate of 30 lbs/min. The paste was allowed to circulate

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for 1 hr with a heating loop on the vessel maintained at 40°C to obtain a slurry. The slurry was feed at a rate of 4 lbs/hr to obtain a total feed of 493 lbs into an esterification vessel which contained a heal from a previous run and was at 250°C. This vessel was equipped with a stirrer and a low boiler column to collect distillates. The temperature was ramped from 250°C to 265°C in 1 hr after feeding all of the ethylene glycol/TPA slurry. The pressure of the vessel was built to 25 psig and maintained. The esterification reaction was allowed to proceed until the level of water in the low boiler column was at a steady state. A portion of the final oligomer was dumped into metal cans and allowed to cool. The final oligomer was ground to 3 to 5 mm particle size. The oligomer had an acid number of 5.40 and was found by analysis to contain 71.43 equivalents carboxyl per million grams. The M_n by GPC was 953 and the M_w by GPC was 1470.

20

Example 2 - Preparation of PET Precursor Using Sb/P Catalyst

The following materials were placed in a stainless steel reactor equipped with a nitrogen inlet, stirrer, and vacuum outlet.

1090 g TPA based oligomer described in Example 1

0.0029 g 1-cyano 6-[4'-(2-hydroxyethyl)anilino]-3H-dibenz[f,ij]isoquinoline-2,7-dione

0.0318 g antimony trioxide

10.2 ml of an ethylene glycol slurry of mixed phosphorus ester compositions (Merpol A) containing 0.07488 g phosphorus

1.4 g of diethylene glycol (2,2'-oxydiethanol)

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The temperature of the reactor and contents was elevated from room temperature to 280°C over a 70 minute time interval with a nitrogen sweep over the reaction mixture. Stirring was begun when the internal
5 temperature of the reaction had reached 220°C. Vacuum was applied at 280°C. The pressure was reduced to 200 torr and was held at 200 torr for 10 minutes. The pressure was reduced to 2.5 torr and the melt phase polycondensation reaction was completed by heating at
10 2.5 torr for 3 hours. The polymer was extruded from the reactor through ice water in a metal trough into a pelletizer to obtain polymer pellets. The pelletized polymer had an inherent viscosity of 0.57 dL/g and was shown by analysis to contain 2 wt % diethylene glycol
15 (DEG).

Example 3 - Solid State Polycondensation of
20 poly(ethylene terephthalate) (PET) from
Example 2

PET polymer pellets (160 g) from Example 2 were crystallized in a 180°C air oven for 45 minutes. The crystallized pellets were placed in a solvent heated
25 glass solid stating apparatus with the nitrogen flow set at 14 SCFH (standard cubic feet per hour). Methyl salicylate was used as the refluxing solvent to yield a solid stating temperature of 222°C to 223°C. The pellets were allowed to polycondense in the solid state
30 for 3 hrs and 25 min. The resulting polymer had an inherent viscosity of 0.72 dL/g and haze half times of 65 and 70 seconds on duplicate samples.

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Example 4 - Preparation of PET Precursor Using Ti/P Catalyst

5 The following materials were placed in a stainless steel reactor equipped with a nitrogen inlet, stirrer, and vacuum outlet.

1090 g TPA based PET oligomer described in Example 1
10 0.0029 g 1-cyano 6-[4'-(2-hydroxyethyl)anilino]-3H-dibenz[f,i]isoquinoline-2,7-dione
1.95 g diethylene glycol
15 0.16 ml acetyltriisopropyl titanate in butanol containing 0.0048 g of Ti
0.6 ml of an ethylene glycol slurry of a mixed ester composition (Merpol A) containing 0.0048 g P
20

The heating, polycondensation, and pelletization were done as described in Example 2 except the final melt phase polycondensation stage was done at 3.25 torr
25 for 3 hours. The final pelletized polymer had an inherent viscosity of 0.58 dL/g and was shown by analysis to contain 1.87 wt % DEG.

30 **Example 5 - Solid State Polycondensation of PET from Example 4**

PET polymer pellets (160 g) from Example 4 were crystallized and allowed to polycondense in the solid
35 state as described in Example 3 except the solid state polycondensation was done for 4 hours and 39 minutes. The resulting polymer had an inherent viscosity of 0.71 dL/g and haze half times of 126 and 132 seconds on duplicate samples.

40 As shown in Table I, polymers prepared by the process described in this invention is useful for

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obtaining a poly(ethylene terephthalate) based polyester with a slow crystallization rate for molding haze preforms which are used to blow mold bottles of different sizes.

5

TABLE 1

Haze Half Times of PET Polymers^a

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Example Number	Catalyst System ^b (ppm)	Haze Half Time ^c (seconds)
Example 3	227 Sb, 78 P	65, 70
Example 5	5 Ti, 6 P	126, 132

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20

- (a) The PET polymers are terephthalic acid based and were prepared using a melt phase polycondensation time of 3 hrs.
- (b) The catalyst levels contained in the polymers were determined by X-ray fluorescence analysis.

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- (c) PET polymers with higher haze half times show less propensity for haze when bottle preforms are molded.

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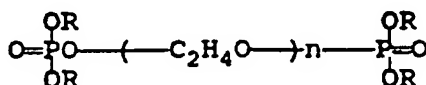
CLAIMS

We claim:

- 5 1. A process of producing a moldable polyethylene
terephthalate or modified polyethylene
terephthalate having an inherent viscosity greater
than 0.65 dL/g comprising:
- 10 reacting a diacid component further comprising
at least 65 mole % terephthalic acid or a diester
component comprising at least 65 mole % C₁ - C₄
dialkyl terephthalate and a diol component
comprising at least 65 mole % ethylene glycol at
temperatures to effect steps (A) and (B) as
15 follows:
- (A) esterification or transesterification,
wherein said esterification is carried
out,
- 20 optionally, in the presence of about
1 to about 50 parts of titanium
present in the form of an alkyl
titanate or
optionally, in the presence of a
catalyst system comprising from
25 about 1 to about 50 parts of
titanium present in the form of an
alkyl titanate and from about 1 to
about 100 parts of phosphorus in the
form of a phosphate ester or
30 phosphoric acid, and
wherein said transesterification is
carried out in the presence of from about
1 to about 50 parts of titanium in the
form of an alkyl titanate; and

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- (B) polycondensation, wherein said polycondensation is carried out in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid; each of the parts of the catalyst representing per million parts of polymer product, wherein the mole percentage for all of the diacid component totals 100 mole %, and wherein the mole percentage for all of the diol component totals 100 mole %.
2. The process of Claim 1 wherein said diacid component comprises at least 95 mole % terephthalic acid and the diol component comprises at least 95 mole % ethylene glycol.
 3. The process of Claim 1 wherein said diacid component is terephthalic acid and said diol component is ethylene glycol.
 4. The process of claim 1 wherein said alkyl titanate is acetyl triisopropyl titanate.
 5. The process of claim 1 wherein said phosphorus-based compound is a phosphate ester.
 6. The process of Claim 5 wherein said phosphate ester has the formula



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5 wherein n has an average value of 1.5 to about 3.0
and each R is selected from the group consisting of
hydrogen or an alkyl radical having from 6 to 10
carbon atoms, wherein the ratio of the number of R
groups or hydrogen atoms to the number of
phosphorus atoms being from about 0.25 to about
0.50 and the ester having a free acidity equivalent
10 of about 0.2 to 0.5.

7. The process of Claim 5 wherein said phosphate
esters comprise ethyl acid phosphate, diethyl acid
phosphate, triethyl acid phosphate, arylalkyl
15 phosphates, tris-2-ethylhexyl phosphate and
mixtures thereof.
8. The process of Claim 1 wherein said phosphorus
compound is phosphoric acid.
- 20 9. The process of Claim 1 wherein said catalyst system
comprises above 1 to about 20 parts of catalyst
metal in the form of alkyl titanate and from about
1 to about 50 phosphorus in the form of said
25 phosphorus compound.
10. The process of Claim 1 wherein said catalyst system
comprises about 3 to about 10 parts of catalyst
metal in the form of an alkyl titanate and from
30 about 5 to about 15 parts of phosphorus in the form
of said phosphorus-based compound.
11. The process of Claim 1 wherein said catalyst system
further comprises an inorganic toner.
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12. The process of Claim 11 wherein said toner further comprises salts of cobalt.
13. The process of Claim 11 wherein said salt of cobalt is cobalt acetate.
14. The process of Claim 13 wherein said cobalt acetate is present in the amount of 10-120 ppm Co, the acetyl triisopropyl titanate is present in the amount of 1-50 ppm Ti, and the phosphorus-based compound is present in the amount of 1-100 ppm P, all parts by weight based on the total weight of the polymer.
15. A process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g comprising reacting
- (a) a diacid or diester component comprising at least 65 mole % terephthalic acid or $C_1 - C_4$ dialkyl terephthalate,
 - (b) a diol component comprising at least 65 mole % ethylene glycol, and
 - (c) an organic toner system comprising about 1 to about 10 ppm of at least one copolymerizable 6-arylamino -1-cyano-3H-dibenz [f,ij] isoquinoline-2,7-dione or at least one copolymerizable 1,4-bis(2,6-dialkylanilino) anthraquinone compound in combination with at least one copolymerizable anthraquinone or red anthrapyridone (6-arylamino-3H-dibenz[f,ij] isoquinoline-2,7-dione) compound at temperatures to effect steps (A) and (B) as follows: (A) esterification or transesterification, wherein said esterification is carried out,

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optionally, in the presence of about 1 to about 50 parts of titanium present in the form of an alkyl titanate or optionally, in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid, and

wherein said transesterification is carried out in the presence of from about 1 to about 50 parts of titanium in the form of an alkyl titanate; and

(B) polycondensation, wherein said polycondensation is carried out in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid;

each of the parts of the catalyst representing per million parts of polymer product, wherein the mole percentage for all of the diacid component totals 100 mole %, and wherein the mole percentage for all of the diol component totals 100 mole %; wherein at least one polyester reactive group is present on each toner component used.

16. The process of Claim 15 where the diacid or diester component comprises at least 95 mole % terephthalic acid or C₁-C₄ dialkyl terephthalate or mixtures thereof and the diol component comprises at least 95 mole % ethylene glycol.

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17. The process of Claim 15 wherein the diacid component is terephthalic acid and the diol component is ethylene glycol.

5 18. The process at Claim 15 wherein the toner comprises at least one 6-arylamino-1-cyano-3H-dibenz [f,i]j isoquinoline-2,7-diones having the formulae

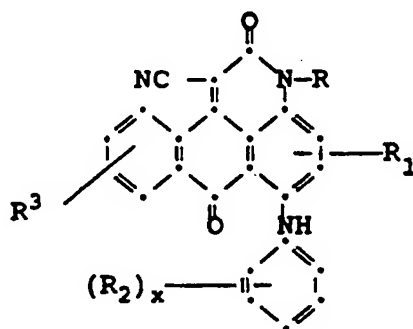
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wherein

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R is hydrogen, cycloalkyl, allyl, alkyl, aryl, aralkyl, alkoxyalkyl or cycloalkylalkylene;

R₁ is hydrogen, halogen, alkyl, alkoxy, aryloxy, alkylthio or arylthio;

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R₂ is hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, carbalkoxy, carbaryloxy, carbaralkoxy, carboxy, sulfamoyl, alkylsulfamoyl, dialkylsulfamoyl, alkylarylsulfamoyl, cycloalkylsulfamoyl, arylsulfamoyl, carbamoyl, alkylcarbamoyl, dialkylcarbamoyl, alkylarylcarmamoyl, cycloalkylcarbamoyl, arylcarbamoyl, 2-pyrrolidono, acylamido, or N-alkylacylamido;

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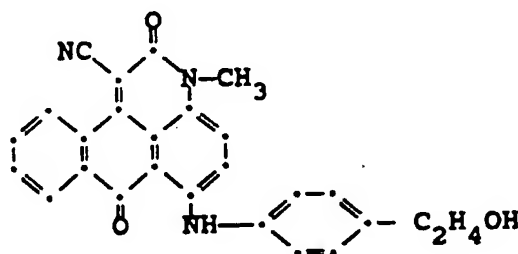
R₃ is one or more residues selected from the group consisting of hydrogen, halogen, alkyl and alkoxy; and

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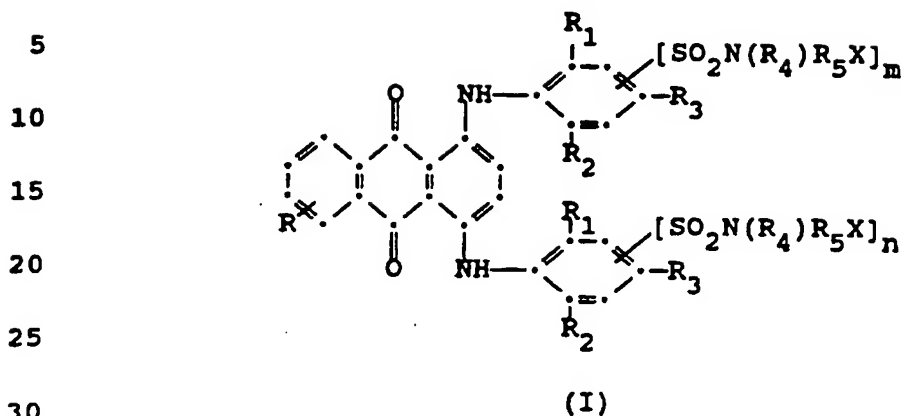
x is an integer of 1 to 5; wherein one or more of the alkyl, alkoxy, alkoxy, aryl, aryloxy, alkylthio, arylthio or aralkyl residues may contain one or more reactive groups selected from the group consisting of carboxy, carbalkoxy, carbaryloxy, N-alkyl-carbamoyloxy, carbamoyloxy, acyloxy, chlorocarbonyl, hydroxyl, cycloalkylcarbonyloxy, N-arylcarbamoyloxy and N,N-dialkylcarbamoyloxy and wherein said alkyl and aryl groups may contain substituents selected from the group consisting of alkoxy, acyloxy, cyano, hydroxy, halogen and acylamido; wherein at least one polyester reactive group is present to permit copolymerization.

19. The process of Claim 17 wherein the toner compound copolymerized is



20. The process of Claim 15 wherein said toner comprises at least one blue 1,4-bis(2,6-dialkylanilino) anthraquinone compound of Formula (I)

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wherein:

R is selected from the group consisting of hydrogen, C₁-C₆ alkyl, halogen, carboxy, and C₁-C₆ alkoxy-C(=O)-;

R₁ and R₂ are independently C₁-C₆-alkyl;

R₃ is selected from the group consisting of hydrogen, halogen, C₁-C₆-alkyl, substituted C₁-C₆ alkyl, hydroxy, C₁-C₆-alkoxy, substituted C₁-C₆-alkoxy, cyano, thiocyanate, C₁-C₆-alkylthio, substituted C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, substituted C₁-C₆-alkylsulfonyl, C₁-C₆-alkoxycarbonyl, carboxy, aryloxy, arylthio, arylsulfonyl, and SO₂N(R₄)R₅X when m and/or n are zero;

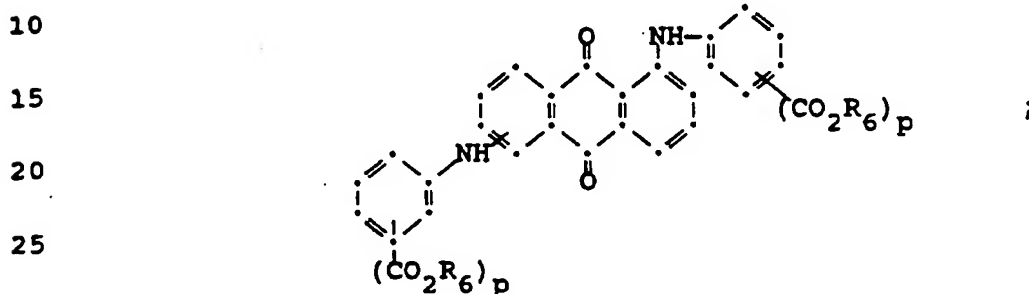
R₄ is selected from the group consisting of hydrogen, C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₃-C₈-alkenyl, C₃-C₈-alkynyl, C₃-C₇-cycloalkyl and aryl;

R₅ is a linking group selected from the group consisting of C₁-C₈-alkylene, C₁-C₆-alkylene-Z-C₁-C₆-alkylene, arylene-C₁-C₆-alkylene, arylene-Z-C₁-C₆-alkylene, C₃-C₇-cycloalkylene, C₁-C₆-alkylene-cycloalkylene-C₁-C₆-alkylene, C₁-C₆-alkylene-arylene-C₁-C₆-alkylene, and C₁-C₆-alkylene-Z-arylene-Z-C₁-C₆-alkylene, wherein Z is selected from -O-, -S- or SO₂;

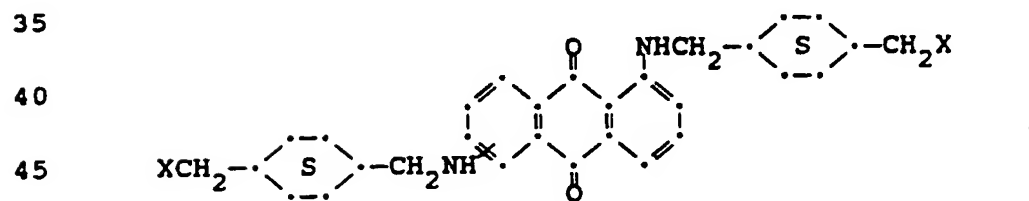
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X is hydrogen or a polyester reactive group; and
 m and n are independently 0 or 1; with the proviso
 that at least one polyester reactive group is present;

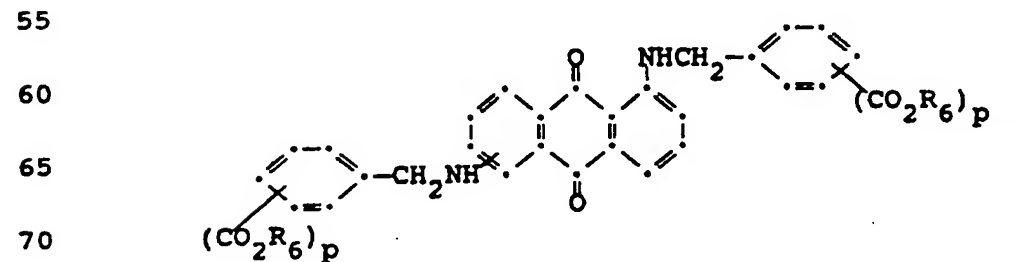
5 along with at least one red anthraquinone or
 anthrapyridone compound selected from formulae
 (II) - (X) below:



II



III



IV

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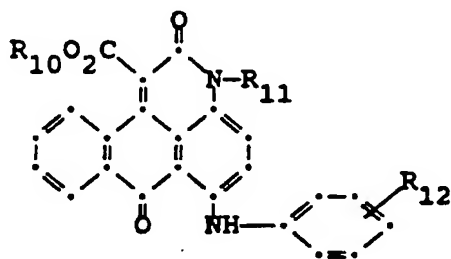
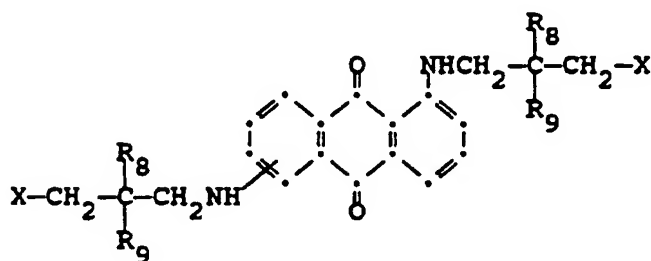
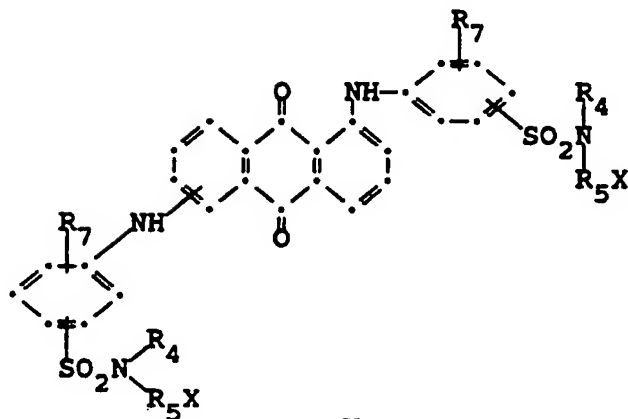
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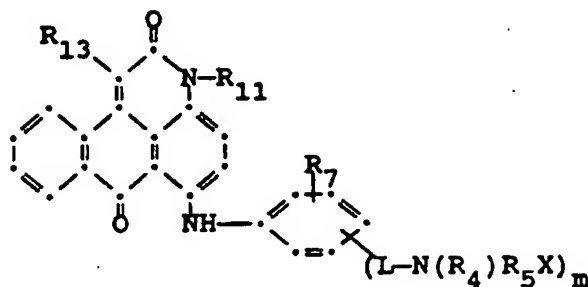
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VIII

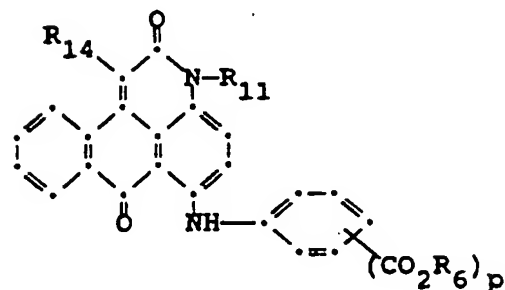
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IX

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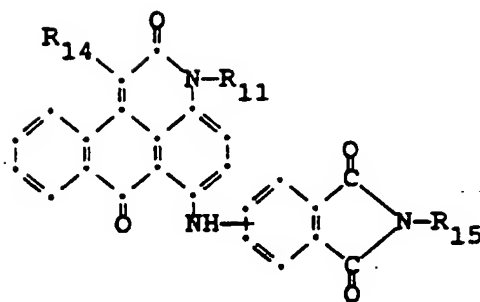
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X

wherein:

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R_6 is selected from the group consisting of hydrogen, C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_3 - C_7 -cycloalkyl or aryl;

R_7 is hydrogen or one to three groups selected from C_1 - C_6 -alkyl, C_1 - C_6 -substituted alkyl, C_1 - C_6 -

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alkanoylamino, halogen, hydroxy C₁-C₆-alkyl,
C₁-C₆-alkoxy, C₁-C₆-alkylthio;

R₈ and R₉ are the same or different and are
selected from the group consisting of C₁-C₆-alkyl,
5 substituted C₁-C₆-alkyl, C₃-C₇-cycloalkyl or aryl;

R₁₀ is selected from the group consisting of
C₁-C₆-alkyl, C₃-C₇-cycloalkyl or aryl;

R₁₁ is selected from the group consisting of
hydrogen, C₁-C₁₂-alkyl, substituted C₁-C₁₂-alkyl,
10 C₃-C₇-cycloalkyl and aryl;

R₁₂ is hydrogen or one to three groups selected
from the group consisting of C₁-C₆-alkyl, substituted
C₁-C₆-alkyl, C₁-C₆-alkoxy, substituted C₁-C₆-alkoxy,
C₁-C₆-alkylthio, substituted C₁-C₆-alkylthio, halogen,
15 hydroxy, C₁-C₆-alkanoylamino, aroylamino, C₁-C₆-
alkylsulfonylamino and arylsulfonylamino;

R₁₃ and R₁₄ are selected from hydrogen, cyano or
CO₂R₁₀;

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R₁₅ is R₄ or R₅X as previously defined;

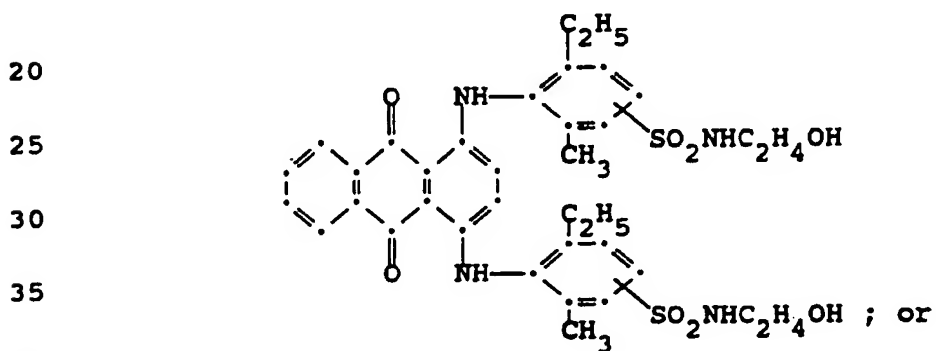
L is -CO- or -SO₂-; X is as previously defined; m
is 0 or 1; and p is 1 or 2; with the provisos that R₁₃
is hydrogen when m is 0 and at least one polyester
25 reactive group is present.

21. The process of Claim 20 wherein the blue
anthraquinone compound(s) correspond to said
structure (I) , wherein R is hydrogen; R₁ and R₂
30 are independently selected from methyl and ethyl;
R₃ is hydrogen, methyl, or bromo; R₄ is hydrogen,
C₁-C₄-alkyl or aryl; R₅ is selected from the group
consisting of C₁-C₆-alkylene,
C₁-C₄-alkylene-O-C₁-C₄-alkylene, -CH₂C₆H₁₀CH₂-,
35 arylene, or -CH₂-arylene- and the red component

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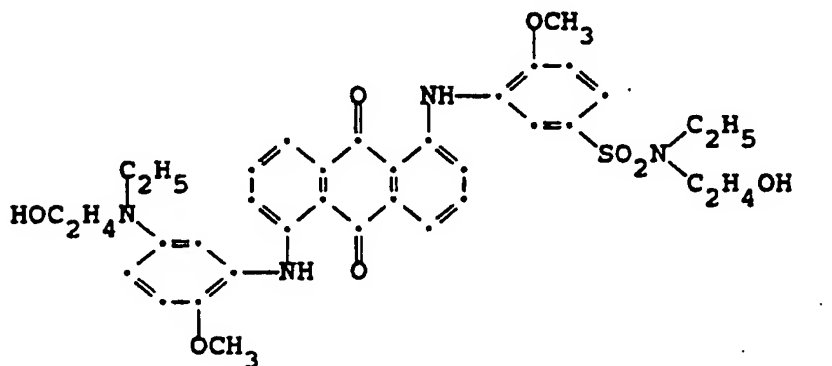
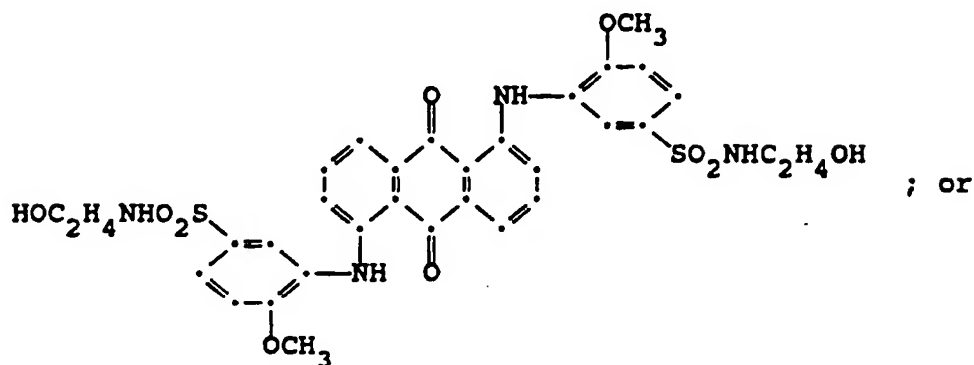
corresponds to formulae (V), wherein R_7 is C_1-C_6 -alkoxy and R_4 and R_5 are as defined in Claim 19.

- 5 22. The process of Claim 21 wherein the concentration of blue and red compounds taken together is from about 1.0ppm to about 10ppm.
- 10 23. The process of Claim 21 wherein the total concentration of blue compound(s) is about 1 to 7ppm and the concentration of red compound(s) is about 1.0 to 3ppm.
- 15 24. The polyester of Claim 21, 22, 23, or 24, wherein the compound of formula (I) is

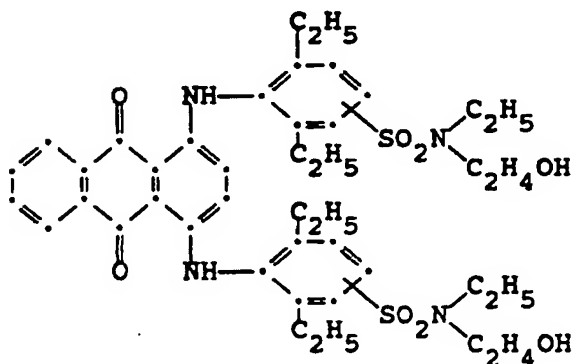


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24. The polyester of Claim 20, 21, 22, 23, or 24 wherein the red compound of formula (V) is

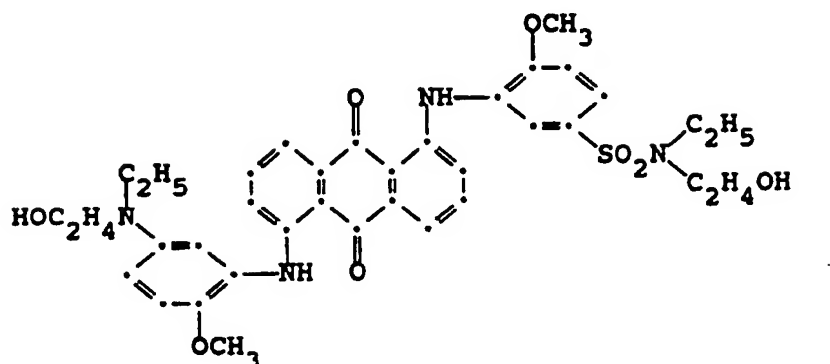


26. The polyester of any one of Claims 20, 21, 22, 23, 24, 25 wherein the blue compound of formula (I) is



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and wherein the red compound of formula (V) is



27. A method for imparting clarity to poly(ethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g comprising reacting at least 95 mole % of terephthalic acid and at least 95 mole % ethylene glycol at a temperature to effect esterification and in the presence of a catalyst system comprising from about 1 to about 20 parts of titanium in the form of an alkyl titanate and from about 1 to about 50 parts of phosphorus in the form of a phosphorus based compound, each of the parts of the components of said catalyst system being per million parts of polymer product.
28. In the method of polymerization, in the melt, of an aromatic polycarboxylic acid or anhydride with a glycol using titanium compound catalysts to form high molecular weight linear polymers, the improvement comprising
- (a) esterifying the acid or anhydride with the glycol in the presence or absence of from about 1 ppm of Ti to about 50 ppm of Ti as an alkyl titanate at a temperature of between

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- about 197°C and about 300°C. for a period of from about 0.5 hours to about 7 hours at a pressure of between about 0 psig and about 100 psig at a molar ratio of glycol to acid or anhydride of about 1.1:1 to about 3:1,
- 5 (b) further reacting and polycondensing the product of step (a), which contains said titanium catalyst, in contact with a phosphorus based compound at about 1 to about 100 ppm phosphorus at a temperature of from about 250 to 310°C, under vacuum of from about 0.1 Torr to about 200 Torr for a period of from about 0.5 hour to 12.0 hours while removing the products of condensation so that the resulting polymer has an intrinsic viscosity between about 0.4 to about 1.2 and contains less than 5 percent by weight diethylene glycol, without adding a diethylene glycol inhibitor, with each of the parts of the compound being per million parts of the first polymer product and
- 10 15 20 25 (c) further polycondensing the crystallized product of step (b) in the solid-state and in the presence of an inert gas or under vacuum and at temperatures of from about 200°C to about 235°C for 2 - 24 hours.

29. A product prepared by the process of Claim 1.

30 30. The product of Claim 29 which is clear.

31. A molded article prepared from moldable poly(ethylene terephthalate) made by the process of Claims 1, 10 and 14.

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32. The molded article of Claim 29 which is a container.

INTERNATIONAL SEARCH REPORT

International Application No

PC/US 95/16378

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RESEARCH DISCLOSURE, vol. 167, no. 010, March 1978, HAVANT GB, page 4 XP002001216 ANONYMOUSLY: "Titanium catalyst for polyester synthesis" see the whole document ---	1-4, 8-14, 29-31
A	US,A,4 250 078 (MCFARLANE ET AL.) 10 February 1981 see claims 1-4; example 8 ---	1,11,15, 20-26
A	US,A,3 907 754 (TERSHANSY ET AL.) 23 September 1975 cited in the application see claims 1-6 --- -/-	1-14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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A document member of the same patent family

Date of the actual completion of the international search

23 April 1996

Date of mailing of the international search report

15.05.96

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Decocker, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16378

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X.	EP,A,0 634 435 (GENERAL ELECTRIC COMPANY) 18 January 1995 see claims 1-9,13-25 -----	1-10

INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 95/16378

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A-3907754	23-09-75	NONE	
EP-A-634435	18-01-95	US-A- 5453479 JP-A- 7138354	26-09-95 30-05-95